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14. ABSTRACT Inverse photoelectron spectroscopy (IPES) has been implemented at the University of Massachusetts Lowell through this ARO-funded DURIP award. The instrumentation consists of a low energy electron gun and a photon detector installed in an ultrahigh vacuum (UHV) chamber. When impinging electrons land in unoccupied electronic states, photons are emitted which contain information regarding the energies of the states. The UHV chamber was already in place at UMass Lowell, and the IPES equipment and associated electronics were added to it. This UHV chamber already had ultraviolet photoelectron spectroscopy (UPS) capability. The combination of UPS and IPES is					
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## Report Title

Final Report: Implementation of Inverse Photoelectron Spectroscopy for Measuring the Empty Electronic States of Metal Oxide Surfaces

### ABSTRACT

Inverse photoelectron spectroscopy (IPES) has been implemented at the University of Massachusetts Lowell through this ARO-funded DURIP award. The instrumentation consists of a low energy electron gun and a photon detector installed in an ultrahigh vacuum (UHV) chamber. When impinging electrons land in unoccupied electronic states, photons are emitted which contain information regarding the energies of the states. The UHV chamber was already in place at UMass Lowell, and the IPES equipment and associated electronics were added to it. This UHV chamber already had ultraviolet photoelectron spectroscopy (UPS) capability. The combination of UPS and IPES in the same instrument makes possible measurements of the energies and densities of filled and empty electronic states. Testing of the instrument is now complete, and initial results on oxidized zirconium have been performed.

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**Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:**

**(a) Papers published in peer-reviewed journals (N/A for none)**

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**TOTAL:**

**Number of Papers published in non peer-reviewed journals:**

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Number of Presentations: 0.00

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**Non Peer-Reviewed Conference Proceeding publications (other than abstracts):**

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Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

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**Peer-Reviewed Conference Proceeding publications (other than abstracts):**

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**TOTAL:**

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

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Received      Paper

**TOTAL:**

Number of Manuscripts:

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TOTAL:

Patents Submitted

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Awards

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<u>NAME</u>	<u>PERCENT SUPPORTED</u>
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Total Number:	

Names of Post Doctorates

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Total Number:	

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
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NAME

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NAME

**Total Number:**

### Names of other research staff

NAME

PERCENT SUPPORTED

**FTE Equivalent:**

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### Sub Contractors (DD882)

### Inventions (DD882)

### Scientific Progress

See attachment

### Technology Transfer

We have strong interactions with the chemical/biological filtration team at the Edgewood Chemical and Biological Center (ECBC). The IPES instrument implemented with funding from this DURIP will help us understand surface chemistry issues of relevance to their research.

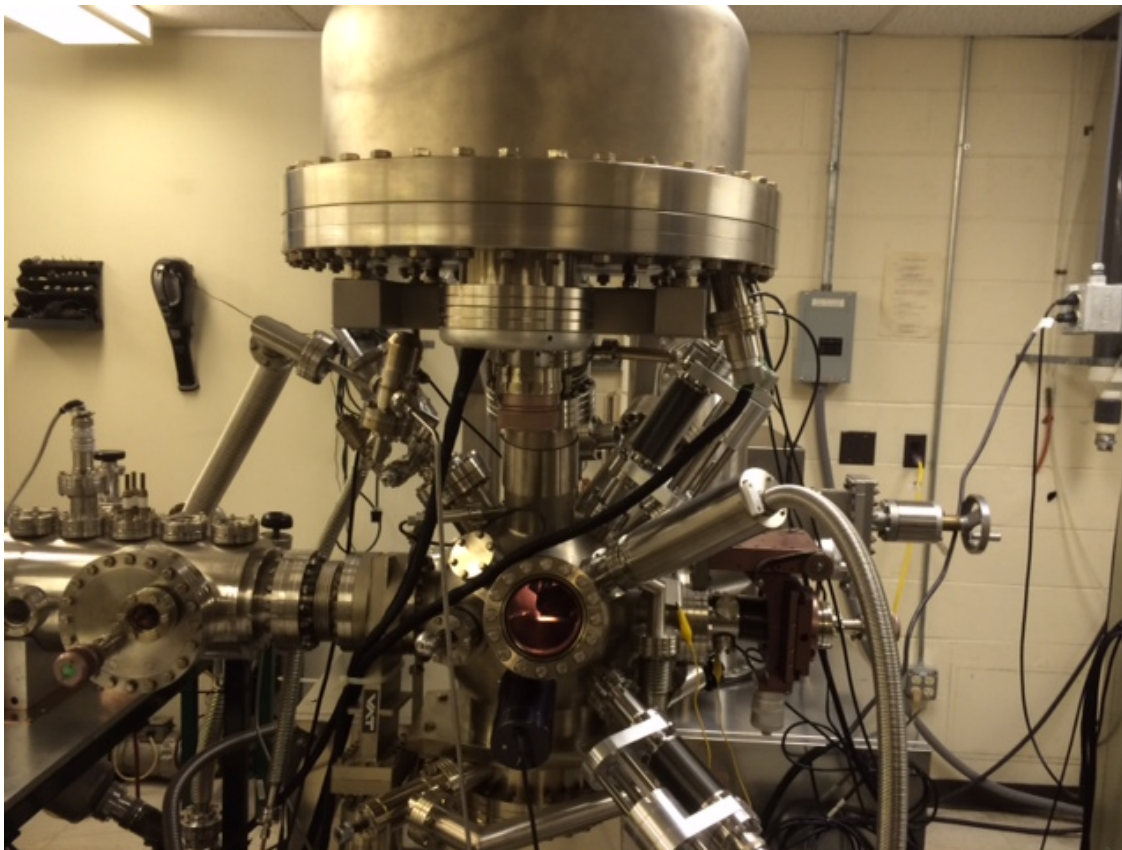
**Final Report**  
DURIP: Implementation of Inverse Photoelectron Spectroscopy  
James E. Whitten (Department of Chemistry)  
The University of Massachusetts Lowell  
Lowell, MA 01854

Inverse photoelectron spectroscopy (IPES) measures the energies and densities of unoccupied orbitals and states on surfaces. In this technique, low energy electrons impinge on a sample and land in empty electronic states. In the Bremsstrahlung isochromat spectroscopy (BIS) mode, impinging electrons in an initial state of energy  $E_{\text{initial}}$  (i.e., the kinetic energy of the electrons) make a transition to an empty, final state of energy  $E_{\text{final}}$ , where  $E_f$  is below the vacuum level. To conserve energy, a photon of energy  $E_{\text{initial}} - E_{\text{final}}$  is emitted. The energy difference between the initial and final states results in the emission of a photon. If the energy of the impinging electron beam is varied, and photons in a narrow band of energy are measured, then the energies of the unoccupied electronic states can be measured. The DURIP grant has allowed us to implement this technique at the University of Massachusetts Lowell.

Major components include a low energy electron gun under the control of a computer and a narrow band photon detector. This equipment and associated electronics were purchased from PSP, Inc. Supporting instrumentation, including an ion gun and turbomolecular pump were also purchased from the DURIP funds. This equipment was installed in an existing photoelectron spectrometer in the Whitten group. The spectrometer into which they were installed already had the capability of performing X-ray and ultraviolet photoelectron spectroscopies (XPS and UPS). XPS is mainly useful for surface chemistry and elemental analysis measurements, and UPS permits measurement of the energies and densities of the filled electronic states. Therefore, the combination of UPS and IPES allows both the filled and empty electronic states to be measured on metal and semiconducting surfaces.

**Figure 1** shows a photograph of the ultrahigh vacuum (UHV) machine that now contains the IPES equipment. The instrument consists of two chambers, with the right one in the photo (the analysis chamber) containing the new equipment. The low energy electron gun and photon detector are aimed at the sample, which is situated in

approximately the center of the right-most chamber. The left chamber contains auxiliary equipment, including a mass spectrometer for thermal desorption and a Kelvin probe.

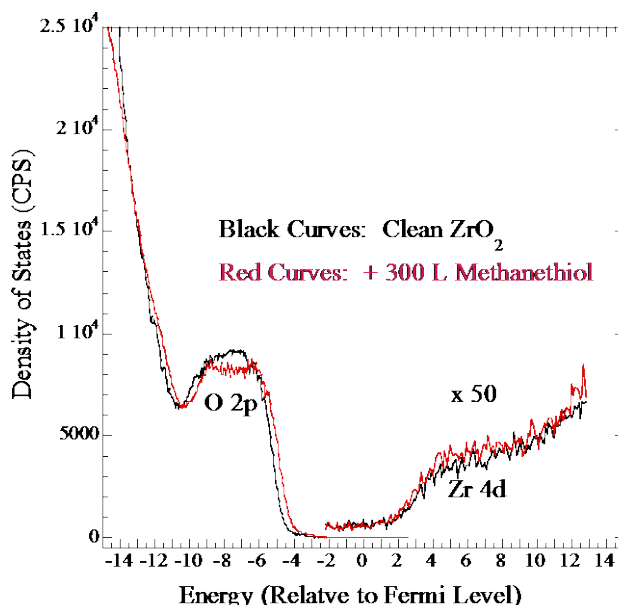


**Figure 1:** Photograph of the photoelectron spectrometer at the University of Massachusetts Lowell into which the IPES equipment has been installed. The low energy electron gun is at the very bottom right of the photo and is on a retractable bellows. The photon detector is not easily visible in the photograph.

The equipment was successfully installed, and initial IPES experiments have been performed. Of particular relevance to ARO/DTRA are measurements of the electronic structure of metal hydroxides and oxides and how this is affected by adsorption of hazardous gases. Ultimately, we are interested in correlating adsorbate-induced changes in the electronic states of the surface with changes in the photoluminescence spectrum.

The results of some of our first experiments on zirconium oxide are shown in **Figure 2**. This figure is a combination of UPS and IPES data, using the instrument in **Figure 1**. The black curves are for unexposed or “clean” zirconium oxide. The occupied valence electronic states are mainly composed of oxygen 2p electrons. The unoccupied states are zirconium 4d electrons. It is

somewhat surprising that methanethiol dosing does not change the spectra more, but there is a change in the filled states, as seen by the shift in the O 2p electrons toward the Fermi level.



**Figure 2:** Combined data from UPS and IPES showing the frontier occupied electronic and near edge unfilled states of oxidized zirconium before and after exposure to 300 L of methanethiol gas. The spectra to the left of zero on the energy scale were measured using UPS, and the spectra to the right of the zero scale were measured with IPES. The IPES curves have been multiplied by 50 for ease of viewing.

The IPES instrument is working well, and more experiments are being performed. These include sputter cleaning zirconium, performing UPS and IPES to measure the band structure, and then leaking in water vapor to adsorb hydroxyl groups. UPS and IPES will then be remeasured. Various gases, including sulfur dioxide, will subsequently be admitted. Our research indicates that  $\text{SO}_3$  replaces the hydroxyl groups and markedly changes the photoluminescence spectrum of particulate  $\text{Zr}(\text{OH})_4$ . It will be important to measure how the IPES and UPS spectra change due to sulfite adsorption. This will increase our knowledge of the mechanisms involved in the observed photoluminescence changes.